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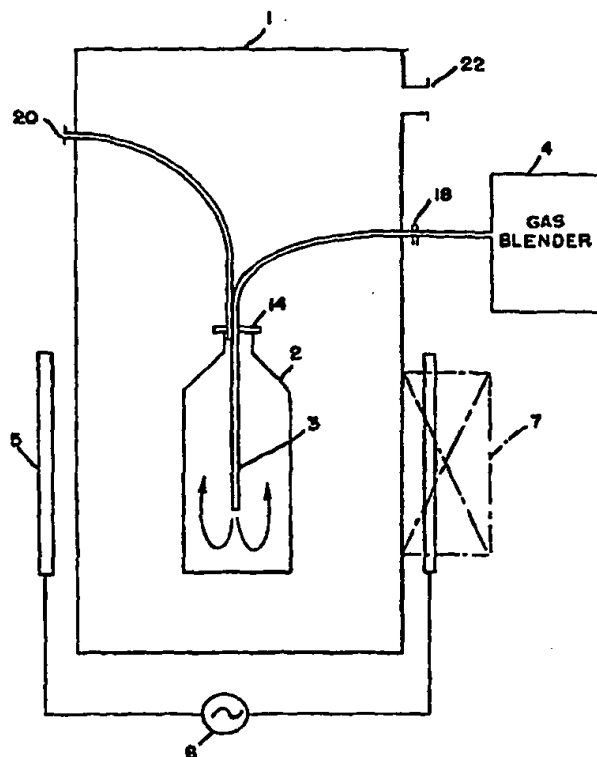
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(54) Title: HOLLOW CONTAINERS WITH INERT OR IMPERMEABLE INNER SURFACE THROUGH PLASMA-ASSISTED SURFACE REACTION OR ON-SURFACE POLYMERIZATION

(57) Abstract

Plasma assisted polymerization and deposition of a very thin inner surface coating in a plastic or metal container without an undesirable increase in container surface temperature is provided to change the surface properties of the internal plastic surface of a container by reaction of the surface with a reactive gas which has been energized to produce a plasma or the surface is activated by a plasma or reactive gas so that it becomes receptive to a further surface reaction. It involves locating the container in an enclosure, inserting means for feeding a reactant gas into the container, selectively controlling the pressure inside the enclosure and inside of the container, cleaning a surface of the container to be coated in situ, pretreating the surface to be coated for enabling a polymer coating subsequently deposited thereon to secure proper adhesion between the coating material and the container material, feeding a reactant gas of predetermined constituency and having barrier properties into the container, generating a plasma of said reactant gas and depositing a relatively thin polymer coating on the surface to be coated, and performing a post polymerization treatment on said polymer coating for eliminating residual monomers and other polymer extractables in situ following deposition of said polymer coating.



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HOLLOW CONTAINERS WITH INERT OR IMPERMEABLE INNER
SURFACE THROUGH PLASMA-ASSISTED SURFACE REACTION
OR ON-SURFACE POLYMERIZATION

BACKGROUND OF THE INVENTION

This invention relates generally to hollow containers with inert and/or impermeable surfaces and more particularly to hollow plastic containers with inert/impermeable inner surfaces produced by plasma assisted in situ polymerization or surface activation.

Plastic and metal containers have been replacing glass in many applications where easy handling, low weight and non-breakability are needed. Where metal is used, the internal metal surface of the container must often be coated with a polymer to avoid contact of the packaged content with the metal. Therefore, in the case of plastic packages, and also in case of many metal containers, the contact surface with the packaged content typically comprises a polymer.

Polymers to date have had varying degrees of inertness to the packaged content which differ from the inertness of glass. In the case of food packages, surface inertness helps diminish potential desorption of packaging material components into the food, to prevent flavor-absorption, to avoid loss of food constituents through the package walls and to avoid ingress of air or other substances from outside the package. All these characteristics of inertness apply to plastic containers; however, some of these characteristics also apply to metal containers which have been internally coated with a plastic or lacquer system.

Refillable plastic packages add a further dimension to inertness requirements because these packages must withstand washing and refilling. Such containers should not absorb contact materials such as washing agents or foreign materials stored in the container.

Packages for carbonated beverages are also normally pressurized and must withstand considerable

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mechanical stress in handling. It is therefore difficult for a single material to provide the necessary mechanical stability and the required inertness.

5 Current plastic packages for carbonated beverages either consist of a single material such as polyethylene terephthalate (PET), or are comprised of multi-layer structures where usually the middle layers provide the barrier properties and the outer layers
10 the mechanical strength properties. Such containers are produced either by co-injection or co-extrusion. To date, plastic containers with an impermeable, dense "glass-like" inner surface have not been able to be produced by conventional methods.

15 Some polymers, e.g. polyacrylonitrile, are known to have exceptional barrier properties, but can only be used in copolymer form because the homopolymer, which has the most ideal barrier properties, cannot be processed in the form of a container. A further
20 limitation in the practical application of polymers for food or beverage containers is that polymers with high barrier properties, again as exemplified by acrylonitrile, tend to have aggressive/dangerous monomers, which implies that their use is limited for
25 food contact unless full polymerization without detectable extractables can be achieved.

 Recycling is yet another dimension with mass produced packages. The reuse of recycled plastic for the same purpose, i.e. to produce new containers by
30 "closed loop" recycling, is an issue which has attracted much attention, and for PET, this has been achieved to date by depolymerizing the recycled material in order to free it of all trace contaminants which might otherwise migrate and come in contact with
35 the container content. An impermeable inner layer, which is the purpose of the invention, would enable

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recycled material to be reused directly for new containers, i.e. without special treatment such as depolymerization since traces of foreign substances could no longer contact the container's content. This would simplify the "closed loop" recycling process considerably by obviating the need for depolymerization.

Furthermore, recyclability within established recycling systems, both "open loop", i.e. recycling for other uses, or "closed loop", i.e. reuse for same purpose, is necessary for any mass produced package. In "open loop" systems, the normal method is to separate, clean and chop up the plastic into small flakes. The flake is then either melted and used for molding other objects or for fiber production. For this type of recycling, it is important that any contaminant to the main plastic, such as a coating, should effectively be present in negligible quantities and, preferably, be solid and insoluble within the molten plastic so that it can be filtered off prior to sensitive applications, such as fiber production. PET is also recycled in "closed loop" systems by depolymerization and it is important that the coating material should be unchanged by this process, be insoluble in the monomers resulting from the process, and be easily separable from these monomers. An inert, thin organic coating or surface treatment which changes the surface composition of PET, fulfills these criteria.

SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide an inner coating or layer for plastic or metal containers, but particularly for refillable plastic containers used for carbonated beverages having the properties of: glass-like impermeability to polar and non-polar substances; elasticity so as to maintain

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coating integrity both when container walls flex/stretch under pressure and when walls are indented; adequate durability and adhesion, during working life, when the inner-surface of container is rubbed, or scuffed, or abraded, for example during filling, pouring or normal use; good transparency so as not to affect the appearance of the clear plastic container; resistance against high/low pH in case of refillable containers for carbonated beverages; safe contact with food for contents such as beverages; and, recyclability of container material without adverse effects.

It is another object of this invention to change the surface properties of a plastic container or of a plastic coating, or of a lacquer, either by surface reaction with a gas or by surface activation and later addition of a surface-changing substance such as a metal ion. The purpose of the surface change is to provide a surface with glass-like inertness/impermeability to polar and non-polar substances, which will withstand the normal rigors of the container e.g. flexing, expansion/contraction abrasion, contact with high/low pH, etc. and not affect container transparency/appearance.

It is a further object of this invention to change the surface properties of a plastic container, as already described, so as to provide the main barrier properties and add a very thin coating, also as described, to enable pH resistance, durability and safe contact with food. This two step method enables greater flexibility in establishing ideal barrier materials without the restrictions imposed by a contact surface while the contact coating is too thin to significantly absorb flavors, or foreign materials placed within the container when this is refillable.

The foregoing and other objects of this invention

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are fulfilled by a method and apparatus to provide for a plasma assisted polymerization and deposition of a very thin inner surface coating in a plastic or metal container and to change the surface properties of the internal plastic surface of a container by reaction of the surface with a reactive gas which has been energized to produce a plasma or the surface is activated by a plasma of reactive gas so that it becomes receptive to a further surface reaction.

The method of forming the polymer coating comprises the steps of: locating the container in an enclosure; inserting means for feeding a reactant gas into the container; selectively controlling the pressure inside the enclosure and inside of the container; cleaning a surface of the container to be coated in situ; pretreating the surface to be coated for enabling a polymer coating subsequently deposited thereon to secure proper adhesion between the coating material and the container material; feeding a reactant gas of predetermined constituency and having barrier properties into the container; generating the plasma of said reactant gas and depositing a relatively thin polymer coating on the surface to be coated; and performing a post polymerization treatment on said polymer coating for eliminating residual monomers and other polymer extractables in situ following deposition of said polymer coating.

In the foregoing process, impermeability to polar and non-polar substances is mainly achieved by: (a) Correct choice of reactive gases or gas mixtures, ionizing (plasma-generating) energy, insert carrier gas mixed with reactive gas(es), vacuum, and gas flow rate, (b) deposition of a dense highly cross-linked polymer substance, in particular, a polymer with high carbon, low hydrogen content. A polymer with a high degree of surface cross linking can be obtained by

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including hydrocarbons with unsaturated bonds, for example acetylene, ethylene etc., as precursors in the reactive gas mixture; (c) deposition of polymers with inorganic radicals such as radicals of halogens, sulphur, nitrogen, metals or silica to assist resistance to absorption of both polar and non-polar substances. These radicals can be brought into the reaction mixture as simple gases e.g. chlorine, fluorine, hydrogen sulphide, as organic complexes e.g. vinylidene dichloride, freons, etc. Silicon and metal radicals can increase absorption resistance to both polar and non-polar substances and can be introduced in gaseous form, for example, as silane (in case of silicon), organic complexes with metals, or volatile metal compounds, in particular hydrides, e.g. SiH_4 , chlorides, fluorides; (d) Depositions of an even, compact coating over the entire surface and particularly avoiding gas inclusion, porosity, surface imperfections. Mechanical design, for example, the gas distribution pipe, rotation of the container etc. can lead to even distribution of plasma over entire surface and coating conditions, particularly deposition rate, are important parameters; (e) Creation of a high quality plasma by optimum use of energy and avoiding energy loss outside container, for example, avoiding formation of a plasma external to container by maintaining different pressures inside the container and outside it; (f) Creation of free radicals on plastic surface so that this surface can react with the reactive gases introduced in plasma state. In this way, increased polymer cross linking, or the inclusion of inorganic radicals can be achieved on the surface of the substrate polymer itself; (g) Creation of free radicals on plastic surface enabling reaction with liquid inorganic substances provide a dense inorganic surface, chemically bound to the

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plastic surface; and, (h) Deposition of several thin layers, each with a specific barrier purpose but so thin that they each have negligible absorption.

Resistance to flexing/stretching is mainly achieved by: (a) Treatment of plastic surface to create free radicals, either before, or during the deposition process, so that deposit is chemically bound to surface. This is done by correct choice of surface activating gas plasma in accordance with the substrate characteristics. For example, argon, oxygen, hydrogen and blends thereof can be used for this purpose; (b) Choice of monomer gas(es) giving target polymers which permit flexing; and (c) Very thin coatings enabling flexing without cracking and achieving flexibility by a narrow cross section.

Adhesion is mainly achieved by: (a) Creation of free radicals on the plastic surface, as above, so that deposit is chemically bound to the plastic surface; (b) Causing a reaction of the plastic surface so as to change its actual composition, as opposed to depositing another substance; and (c) Effective surface cleaning during or before main treatment using ionized gas (gas plasma), such as oxygen, to remove surface contaminants.

pH resistance and inertness to contents and transparency are mainly achieved by: (a) Correct choice of substance deposited through choice of reactive gas(es), inert carrier gas(es), ionizing (plasma generating) energy, vacuum, and gas flow rate; and (b) Post treatment with gas plasma to remove unreacted monomers and to saturate unreacted free radicals on the surface.

Apparatus for performing the aforementioned method steps comprise: means for locating the container in the vacuum chamber; means for feeding a reactant gas or a mixture of gases into the container;

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means for controlling the pressure inside the vacuum chamber; means for controlling the pressure inside of the container; means for cleaning a surface of the container to be coated in situ and pretreating the surface for enabling a polymer coating subsequently deposited thereon to secure proper adhesion between the coating material and the container material; and means for feeding a reactant gas of predetermined constituency and having the capability of reacting to provide high barrier properties in the container for generating a plasma of said reactant gas and depositing a relatively thin polymer coating on the surface to be coated, and thereafter performing a post polymerization treatment on said polymer coating, such as by applying a high-energy source, and for eliminating residual monomers and other polymer extractables in situ following deposition of said polymer coating.

The method of changing the surface composition comprises the steps of: (a) locating a formed container in a vacuum chamber; (b) inserting means for feeding a reactant gas into the container; evacuating the vacuum chamber; (c) feeding a reactant gas or a mixture of gases of a predetermined type into the container; and (d) generating a plasma of said reactant gas for causing a change in the surface composition of the inner surface of said container where the reactant gas is of a type to cause a direct change in surface properties of said plastic inner surface or is of a type to activate the plastic inner surface to enable a reaction of the plastic surface with inorganic materials so as to make the inner plastic surface inert/impermeable.

Apparatus for performing the latter method steps includes: means for locating a formed container in a vacuum chamber; means for feeding a reactant gas into

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the container; means for evacuating the vacuum chamber; means for feeding a reactant gas of a predetermined type into the container; and means for generating a plasma of said reactant gas for causing a change in the surface composition of the inner surface of said container where the reactant gas is of a type to cause a direct change in surface properties of said plastic inner surface or is of a type to activate the plastic inner surface to enable a reaction of the plastic surface with inorganic materials so as to make the inner plastic surface inert/impermeable.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be more readily understood from the detailed description provided hereinbelow and the accompanying drawings which are provided by way of illustration only, and thus are not limitative of the present invention and wherein:

Figure 1 is an electro-mechanical schematic diagram broadly illustrative of the invention;

Figure 2A is a central longitudinal cross sectional view of the preferred embodiment of the invention;

Figure 2B is a partial cross-sectional view of a modification of the gas tube shown in Figure 2A;

Figure 2C is a modified version of the embodiment in Figure 2A which enables the container to be rotated;

Figure 3 is a diagram illustrative of a method which is implemented by the apparatus shown in Figures 1 and 2; and

Figure 4 is a diagram showing another method which can be implemented by the apparatus shown in the Figures.

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DETAILED DESCRIPTION OF THE INVENTION

Referring now to the drawings, Figure 1 is broadly illustrative of the inventive concept of this invention. There a high vacuum enclosure 1 encloses the container 2 to be coated. A metal gas pipe 3 or other type conductor is located in and dips into the base of the container 2 where it ducts gas into the container 2 from a gas blending system 4. The gas flowing into container 2 is a blend of gases energized externally either by a high frequency coil 5 and generator 6 or by a microwave generator 7. One option (not shown) is to connect one terminal of generator 6 to the metal gas pipe 3, thus using it as an electrode and reducing energy losses in plasma generation by having one electrode in direct contact with the plasma.

A further option, not shown, which is particularly applicable for low vacuum operation, is to apply a high DC potential and produce an electrical discharge between metal gas pipe 3 and a grounded terminal outside the container 2, such as the walls of enclosure 1.

In a first method, gas of a predetermined constituency is supplied from the blender 4 which is programmed to first provide a cleansing plasma energized gas stream at the beginning of a coating cycle, before reaction gases are introduced into the system. By the correct selection of the gas blend and by energizing the gas blend to form a plasma, free radicals formed thereby are induced at the inner surface of the container before the reactant gases are introduced. After cleaning and surface activation, where necessary, the cleansing/surface preparation gas blend is switched to a gas blend which provides in situ plasma assisted polymerization. An after treatment of the coating is completed to eliminate

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monomers and other polymer extractables using the high energy sources of electromagnetic energy 6 or 7 with or without a suitable plasma energized reactant gas from the blender 4.

5 Plasma assistance secures a clean surface, free of dust and dirt and furthermore enables a wide range of polymerizations, so that the coating polymer can be customized for inertness. Use of very thin coating further enables flexibility and also transparency
10 where the polymer has poor transparency properties. To enable use with heat sensitive plastic containers, the invention also provides for coating without unacceptable increase in substrate surface temperature.

15 In a second method, the gas blend flowing into container 2 is selected to provide surface reaction(s) and is energized externally either by the high-frequency generator 5, or by the microwave generator 7, or by a high DC potential causing electrical
20 discharge, as described above. Where the surface reaction is intended simply to provide a surface activation preparatory to the subsequent reaction and grafting to plastic surface of gaseous substances, such as inorganic gases, these substances are blended
25 by the blending system 4 and introduced after the surface activation stage already described. Alternatively, where the substances to be added to the activated surface are in liquid form, as for example in case of metal ions, these liquid reactive
30 substances can be introduced at a later stage by a conventional liquid-filling process.

 The inside of the container 2 is connected to a controlled vacuum source, not shown, via a cap 14 which also acts to seal the container opening with a
35 tube coupled to a vacuum connector 20. The outside of the container 2 is connected to a second controlled

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vacuum source, not shown, by means of vacuum connector 22. This enables a vacuum to be applied within the enclosure 1 which is different and independent of the vacuum applied inside container 2 and thus enables proper adjustment of plasma production conditions.

The apparatus described above and shown in Figure 1 has the capability of providing the following conditions with a view to providing a polymer coating of optimal integrity under stress and with ideal inertness and barrier properties: (1) completeness of coating by pre-cleaning the inner surface of the container using a plasma energized gas; (2) coating adhesion by pretreating the container surface to produce free radical using plasma energized gas, thereby enabling the coating to resist flexing, stretching, indenting, etc.; (3) in situ polymerization of coating which avoids the need to remelt the polymer which in turn limits the range of potential polymers in normal coating applications. Avoiding remelting also avoids depolymerization by-products, and thus potential extractables, therefore improving inertness; (4) in situ free monomer elimination by means of an after treatment, using either an energizing source or a plasma energized reactive gas; (5) separate control of pressure inside and outside container and separate control of gas blend and energizing conditions for each coating phase, so as to provide best conditions for each of the functions alluded to above; (6) very thin coatings, e.g. 25-1500nm, thereby promoting flexibility, transparency and elimination of extractables; (7) a wide choice of polymerization conditions and a wide range of resulting polymers which are enabled through correct choice of gases, vacuum, and energy input,; and (8) which by correct choice of conditions of vacuum, gas flow and energy

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input avoids unacceptable heating of the substrate surface, thus enabling use for heat sensitive containers, such as orientated PET.

Also, this apparatus has, with a view to changing
5 the internal surface of a plastic or plastic-coated container, either directly by surface reaction, or by surface activation which enables subsequent surface reaction, the capability of: (1) through correct
10 choice of gases, vacuum and energy input, enabling a wide range of surface reactions; (2) controlling the surface temperature and a surface temperature so that its rise, if any, is limited to that acceptable by heat-sensitive, orientated containers, such as PET; and (3) providing a process which can be used for any
15 plastic and any container, after forming the container, and which is independent of the container-forming machine.

Referring now to Figure 2A, shown thereat are further details of the vacuum chamber 1 which
20 additionally comprises: a container elevator 10, a vacuum sleeve 11 which is fitted with spring 12, sliding sealing rings 15, rubber sealing ring 16, and a vacuum sleeve head 13.

Container 2 is adapted to be pushed upwards by
25 the elevator 10 until its progress is stopped by sealing ring 14 which seals the container opening. The container 2 is centered and guided by an annular sliding guide 25. The spring loaded assembly of the vacuum sleeve 11 is secured by cap 17 which also
30 precompresses the spring 12 and connects to the vacuum sleeve head 13. One or more pins 26 ensure that the sliding bottle guide 25 remains in place. The vacuum sleeve head 13 is connected to a bracket 27 supporting the gas tube 3.

35 In addition, the bracket 27 has a distributor pipe 22 for the vacuum source external to container 2,

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and a distributor pipe 20 for the vacuum source internal to the container 2. These elements are connected via control valves 23 and 21, respectively. Control valves 23 and 21 enable vacuum to be applied by a sequence controller 24 as soon as the opening of container 2 seals against seal 14, and to release vacuum when container 2 is ready for removal from device. Bracket 27 also has gas distributor 18 which couples from the gas blender 4 to the gas pipe 3 via an on-off valve 19 which is connected to and controlled by sequence controller 24.

Sequence controller 24 in connection with a machine cam, not shown, is mechanically connected to a machine timing apparatus. It also sequences the switching of the plasma generator 6 or 7. The dip tube 3 when desirable can be configured to be fitted with a mantle 3a as shown in Figure 2B to permit improved distribution of gas to the sides of container 2.

Figure 2C depicts the coating device described by Figure 2A but now with the additional facility of rotating the container 2. The container 2 rests on a freely-rotating steel platform 35, in which a permanent magnet, not shown, is embedded and which is made to rotate by an external electromagnetic field generated by an electromagnet 36. At the top of container 2, the sealing ring 14 is mounted on a rotatable sleeve 37, which is free to rotate within a recess 38 and a pair of sealing rings 39.

Figure 3 depicts one method of operation of the apparatus shown in Figure 2A. The apparatus shown is a well known "carousel" or rotating type system, and is comprised of at least four coating cells 1a, 1b, 1c and 1d, located at stations A, B, C and D, each including a vacuum sleeve 11 and vacuum sleeve head 13.

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At station A, a pusher 30 or other similar device brings container 2 onto an elevator 10 where the container 2 is then pushed up into a chamber formed by the vacuum sleeve 11 and sleeve head 13. At stations
5 B and C, the sequence controller 24 activates the evacuation valves 21 and 23, the gas injection valve 19 and plasma generation means 7 or when desirable, means 6 shown in Figure 1 in the appropriate order for the coating cycle. At station D, the elevator 10
10 withdraws and container 2 is ejected. The container handling details, either in a rotating "carousel" type of machine as described, or in lanes, or with other appropriate means, is incidental to the invention and can be implemented as desired.

15 Since certain coating options for container 2 could involve several layers and coating operations, it may be impracticable to carry them out in the rotating "carousel" type machine, illustrated by Fig. 3. Figure 4 illustrates a further embodiment where
20 coating times and coating operations of multiple containers can be implemented simultaneously.

As shown, container 2 is transported by conveyor belt 40. A row of containers 2 are then gripped by grippers 41 and placed in treatment vessel 42 where
25 they are firmly located by the shape of the partitions in a treatment vessel 42. In the embodiment shown, a pusher 43 raises the treatment vessel 42 to a treatment head 44 which trips and tightly seals the top of treatment vessel 42. The treatment head 44
30 includes a multiplicity of all the coating facilities described by Fig. 3, in particular the gas distributor 18, vacuum distribution pipes 20 and 22.

Each individual container 2 in treatment vessel 42 can be rotated by the manner described by Fig. 2A.
35 After coating treatment, the coating head 44 moves to a further position where it releases treatment vessel

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42 where it is returned to an unloading position by
pusher 45. The containers 2 are then unloaded by
grippers 46 onto a finished goods conveyor belt 47.
The empty treatment vessel 42 is now returned by
5 pusher 48 to receive fresh load of container 2 from
gripper 41.

There is a plurality of treatment vessels 42 and
treatment head(s) 44 according to production needs,
and the cycle can operate either by raising the
10 treatment vessels 42 to the treatment head(s) 44, as
shown, or by conveying the treatment vessel 42
horizontally to one or several treatment positions and
lowering one or several treatment heads 44 to the
treatment vessel 42.

15 The container or treatment vessel handling
details, be it in a "carousel" type drive as shown in
Fig. 3, or in a linear device as shown in Fig. 4, are
state-of-the-art and accordingly are incidental to
this invention. The invention intends only to
20 demonstrate the principles as illustrated by Fig. 3
and Fig. 4. These are essential to enable containers
to be processed by practical means at high speed,
while giving the flexibility of coating parameters
required to produce the high quality coating criteria
25 described.

Having thus shown and described what is at
present considered to be the preferred embodiment of
the invention, it should be noted that all
modifications, alterations and changes coming within
30 the spirit and scope of the invention as set forth in
the appended claims are herein meant to be included.

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CLAIMS

1 1. A method of forming a polymer coating on a
2 surface of a container without an undesirable increase
3 in container surface temperature, comprising the steps
4 of:

5 (a) locating the container in an enclosure;

6 (b) inserting means for feeding a reactant gas
7 into the container;

8 (c) selectively controlling the pressure inside
9 the enclosure and inside of the container;

10 (d) cleaning a surface of the container to be
11 coated in situ;

12 (e) pretreating the surface to be coated for
13 enabling a polymer coating subsequently deposited
14 thereon to secure proper adhesion between the coating
15 material and the container material;

16 (f) feeding a reactant gas of predetermined
17 constituency and having barrier properties into the
18 container;

19 (g) generating a plasma of said reactant gas and
20 depositing a relatively thin polymer coating on the
21 surface to be coated; and

22 (h) performing a post polymerization treatment
23 on said polymer coating for eliminating residual
24 monomers and other polymer extractables in situ
25 following deposition of said polymer coating.

1 2. The method of claim 1 wherein said cleaning
2 step (d) comprises feeding a reactant gas of
3 predetermined constituency and having cleaning
4 properties into said container and generating a plasma
5 thereof.

1 3. The method of claim 1 wherein said
2 pretreating step (e) comprises feeding a reactant gas
3 of predetermined constituency and having surface

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4 activation properties into said container and
5 generating a plasma thereof for producing free
6 radicals for enhancing coating adhesion to the surface
7 to be coated.

1 4. The method of claim 1 wherein said step (g)
2 of generating a plasma includes the use of microwaves,
3 of relatively high frequency AC energy or a DC
4 discharge.

1 5. The method of claim 1 wherein said post
2 polymerization treatment step (h) comprises applying
3 electromagnetic energy to said polymer coating from a
4 relatively high energy source.

1 6. The method of claim 1 wherein said post
2 polymerization treatment step (h) comprises feeding a
3 reactant gas of predetermined constituency into said
4 container and generating a plasma.

1 7. The method of claim 1 wherein said depositing
2 step (g) comprises depositing a polymer coating having
3 a thickness ranging between 25nm and 1500nm whereby
4 transparency, flexibility and relative ease of
5 elimination of residual monomers and polymer
6 extractables are provided.

1 8. The method of claim 1 wherein said surface to
2 be coated comprises the inside surface of said
3 container.

1 9. The method of claim 1 wherein said container
2 comprises a plastic container.

1 10. The method of claim 1 wherein said container
2 comprises a narrow mouthed plastic container.

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1 11. The method of claim 1 wherein said container
2 comprises a narrow mouthed container formed from
3 polyethylene terephthalate.

1 12. A method of forming a polymer coating on a
2 surface of a container without an undesirable increase
3 in container surface temperature, comprising the steps
4 of:

5 (a) locating the container in a vacuum chamber:

6 (b) inserting means for feeding a reactant gas
7 into the container;

8 (c) selectively controlling the pressure inside
9 the vacuum chamber and inside of the container;

10 (d) cleaning a surface of the container to be
11 coated in situ by feeding a reactant gas of
12 predetermined constituency and having cleaning
13 properties into said container and generating a plasma
14 thereof;

15 (e) pretreating the surface to be coated by
16 feeding a reactant gas of predetermined constituency
17 and having surface activation properties into said
18 container and generating a plasma thereof for
19 producing free radicals for enhancing coating adhesion
20 between the surface to be coated and the container;

21 (f) feeding a reactant gas of predetermined
22 constituency and having barrier properties into the
23 container;

24 (g) generating the plasma of said reactant gas
25 having barrier properties and depositing a relatively
26 thin polymer coating on the surface to be coated; and

27 (h) performing a post polymerization treatment
28 on said polymer coating for eliminating residual
29 monomers and other polymer extractables in situ
30 following deposition of said polymer coating by
31 applying electromagnetic energy to said polymer
32 coating from a relatively high energy source or

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33 feeding a reactant gas of predetermined constituency
34 into said container and generating a plasma thereof.

1 13. A system of forming a polymer coating on a
2 surface of a container without an undesirable increase
3 in container surface temperature, comprising:

4 (a) means for locating the container in an
5 enclosure;

6 (b) means for feeding a reactant gas into the
7 container;

8 (c) means for controlling the pressure inside
9 the enclosure; and

10 (d) means for controlling the pressure inside of
11 the container;

12 (e) means for cleaning a surface of the
13 container to be coated in situ;

14 (f) means for pretreating the surface to be
15 coated for enabling a polymer coating subsequently
16 deposited thereon to secure proper adhesion between
17 the coating material and the container material;

18 (g) means for feeding a reactant gas of
19 predetermined constituency and having barrier
20 properties into the container;

21 (h) means for generating a plasma of said
22 reactant gas having barrier properties and depositing
23 a relatively thin polymer coating on the surface to be
24 coated; and

25 (i) means for performing a post polymerization
26 treatment on said polymer coating for eliminating
27 residual monomers and other polymer extractables in
28 situ following deposition of said polymer coating.

1 14. The system of claim 13 wherein said
2 enclosure comprises a vacuum chamber.

1 15. The system of claim 13 wherein said means

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2 for cleaning comprises means for feeding a reactant
3 gas of predetermined constituency and having cleaning
4 properties into said container and means for
5 generating a plasma thereof.

1 16. The system of claim 13 wherein said means
2 for pretreating comprises means for feeding a reactant
3 gas of predetermined constituency and having surface
4 activation properties into said container and means
5 for generating a plasma thereof for producing free
6 radicals for enhancing coating adhesion to the surface
7 to be coated.

1 17. The system of claim 13 wherein said post
2 polymerization treatment means comprises means for
3 applying electromagnetic energy to said polymer
4 coating from a relatively high energy source.

1 18. The system of claim 13 wherein said post
2 polymerization treatment means comprises means for
3 feeding a reactant gas of predetermined constituency
4 into said container and means for generating a plasma.

1 19. The system of claim 13 wherein said
2 depositing means comprises means for depositing a
3 polymer coating having a thickness ranging between
4 25nm and 1500nm whereby transparency, flexibility and
5 relative ease of elimination of residual monomers and
6 polymer extractables are provided.

1 20. The system of claim 13 wherein said surface
2 to be coated comprises the inside surface of said
3 container.

1 21. The system of claim 13 wherein said
2 container comprises a narrow mouthed plastic

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3 container.

1 22. A system for forming a polymer coating on a
2 surface of a plastic beverage container, comprising:

3 (a) a vacuum chamber;

4 (b) means for transporting the container to and
5 from the vacuum chamber;

6 (c) means for selectively controlling the
7 pressure inside the vacuum chamber and inside of the
8 container;

9 (d) means for cleaning a surface of the
10 container to be coated in situ comprising means for
11 feeding a first reactant gas of predetermined
12 constituency and having cleaning properties into said
13 container;

14 (e) means for generating a plasma of said first
15 reactant gas;

16 (f) means for pretreating the surface to be
17 coated comprising means for feeding a second reactant
18 gas of predetermined constituency and having surface
19 activation properties into said container and
20 generating a plasma thereof for producing free
21 radicals for enhancing coating adhesion between the
22 surface to be coated and the container;

23 (g) means for feeding a third reactant gas of
24 predetermined constituency and having barrier
25 properties into the container;

26 (h) means for generating a plasma of said third
27 reactant gas and depositing a relatively thin polymer
28 coating on the surface to be coated; and

29 (i) means for performing a post polymerization
30 treatment on said polymer coating for eliminating
31 residual monomers and other polymer extractables in
32 situ following deposition of said polymer coating
33 comprising means for applying electromagnetic energy
34 to said polymer coating from a relatively high energy

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35 source or means for feeding a fourth reactant gas of
36 predetermined constituency into said container and
37 generating a plasma thereof.

1 23. A method of forming an inert/impermeable
1 inner surface of a container having a plastic inner
2 surface without an undesirable increase in container
3 surface temperature, comprising the steps of:

4 (a) locating a formed container in a vacuum
5 chamber;

6 (b) inserting means for feeding a reactant gas
7 into the container;

8 (c) evacuating the vacuum chamber;

9 (d) feeding a reactant gas of a predetermined
10 type into the container; and

11 (e) generating a plasma of said reactant gas for
12 causing a change in the surface composition of the
13 inner surface of said container.

1 24. The method of claim 23 wherein said reactant
2 gas is of a type to cause a direct change in surface
3 properties of said plastic inner surface so as to make
4 said surface inert/impermeable.

1 25. The method of claim 23 wherein said reactant
2 gas is of a type to activate the plastic inner surface
3 to enable a reaction of the plastic surface with
4 inorganic materials so as to make the inner plastic
5 surface inert/impermeable.

1 26. The method of claim 25 and additionally
2 including the step of introducing a predetermined
3 inorganic substance to the inner surface of the
4 container.

1 27. The method of claim 25 and additionally

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2 including the step of introducing a solution of metal
3 ions to the inner surface of the container.

1 28. A system for forming an inert/impermeable
2 inner surface of a container having a plastic inner
3 surface without an undesirable increase in container
4 surface temperature, comprising the steps of:

- 5 (a) a vacuum chamber;
6 (b) means for transporting a formed container to
7 and from said vacuum chamber;
8 (c) means for controlling the pressure or vacuum
9 in the vacuum chamber;
10 (d) means for feeding a reactant gas of a
11 predetermined type into the container; and
12 (e) means for generating a plasma of said
13 reactant gas for causing a change in the surface
14 composition of the inner surface of said container.

1 29. The system of claim 28 wherein said reactant
2 gas comprises a gas causing a direct change in surface
3 properties of said plastic inner surface so as to make
4 said surface inert/impermeable.

1 30. The system of claim 28 wherein said reactant
2 gas comprises a gas for activating the plastic inner
3 surface to enable a reaction of the plastic surface
4 with inorganic materials so as to make the inner
5 plastic surface inert/impermeable.

1 31. The system of claim 30 wherein said gas
2 includes a predetermined inorganic substance.

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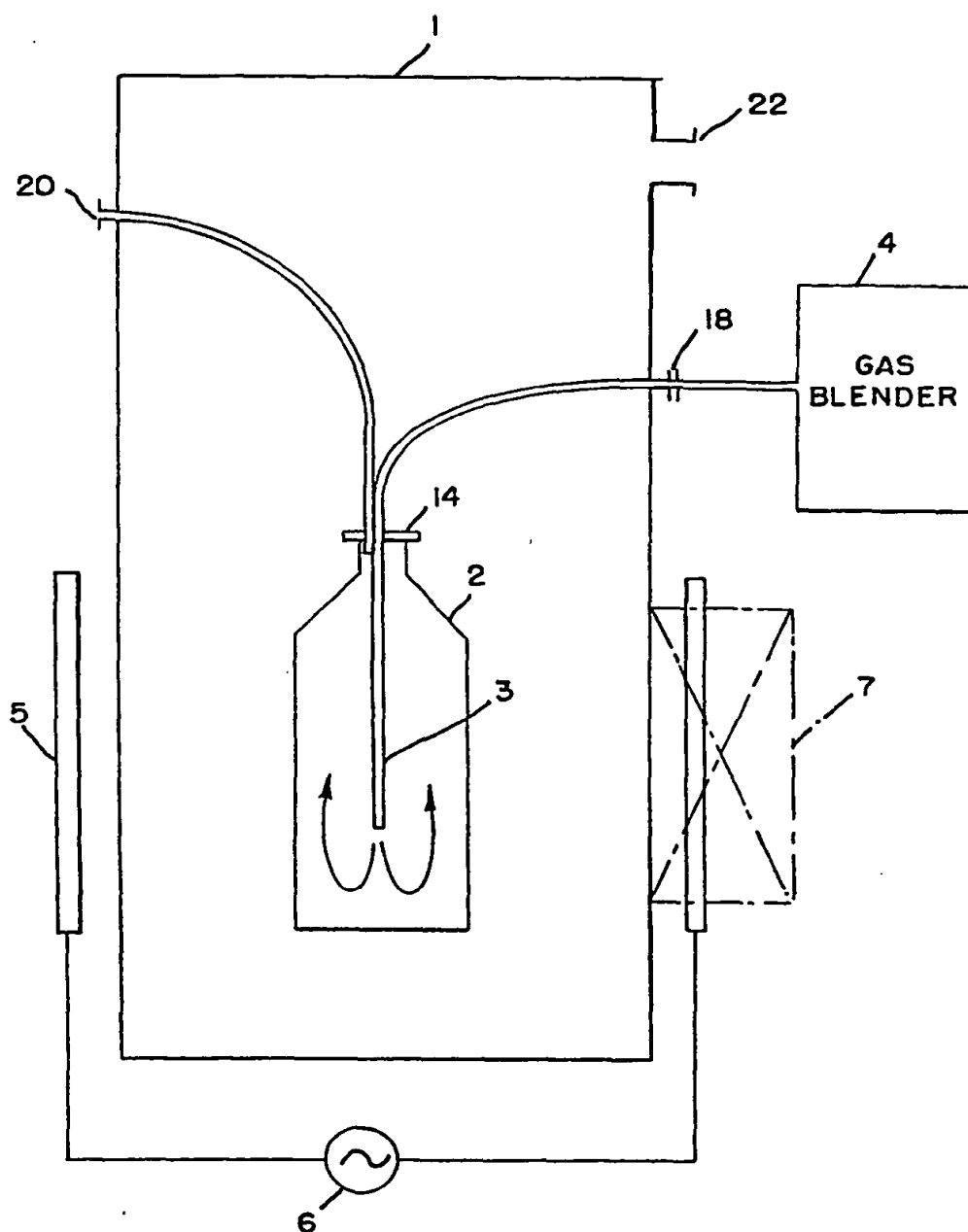


FIG. 1

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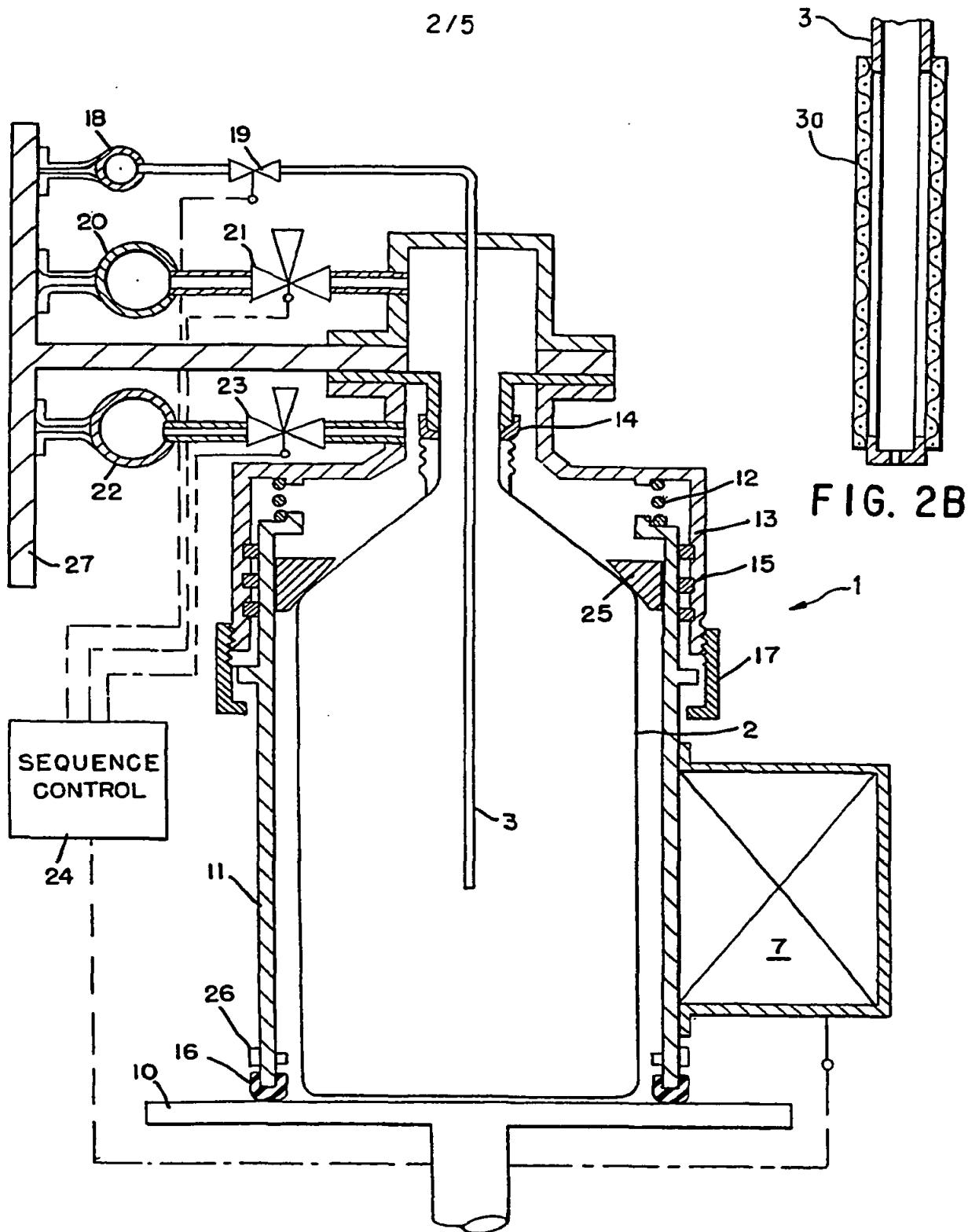


FIG. 2B

FIG. 2A

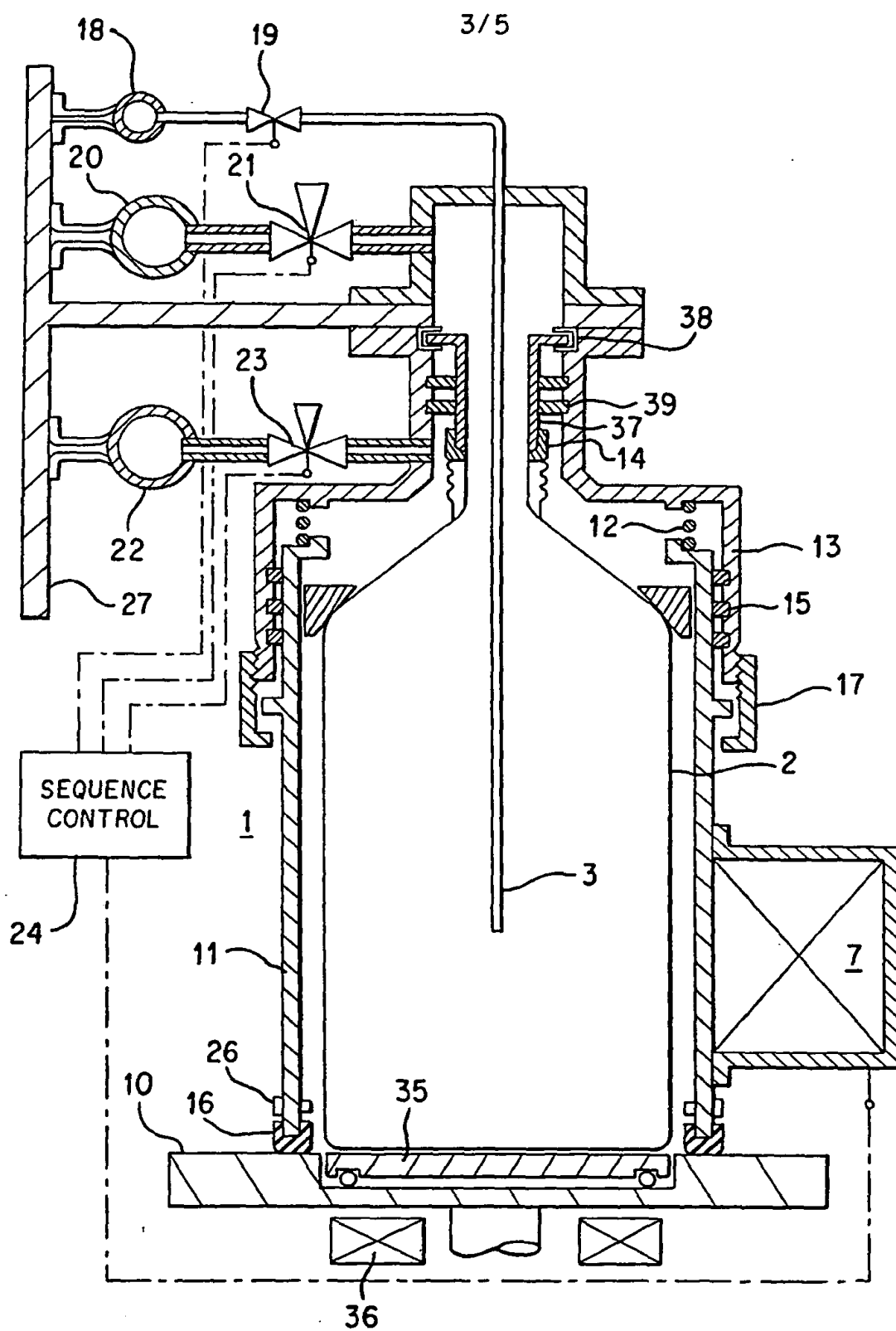


FIG. 2C

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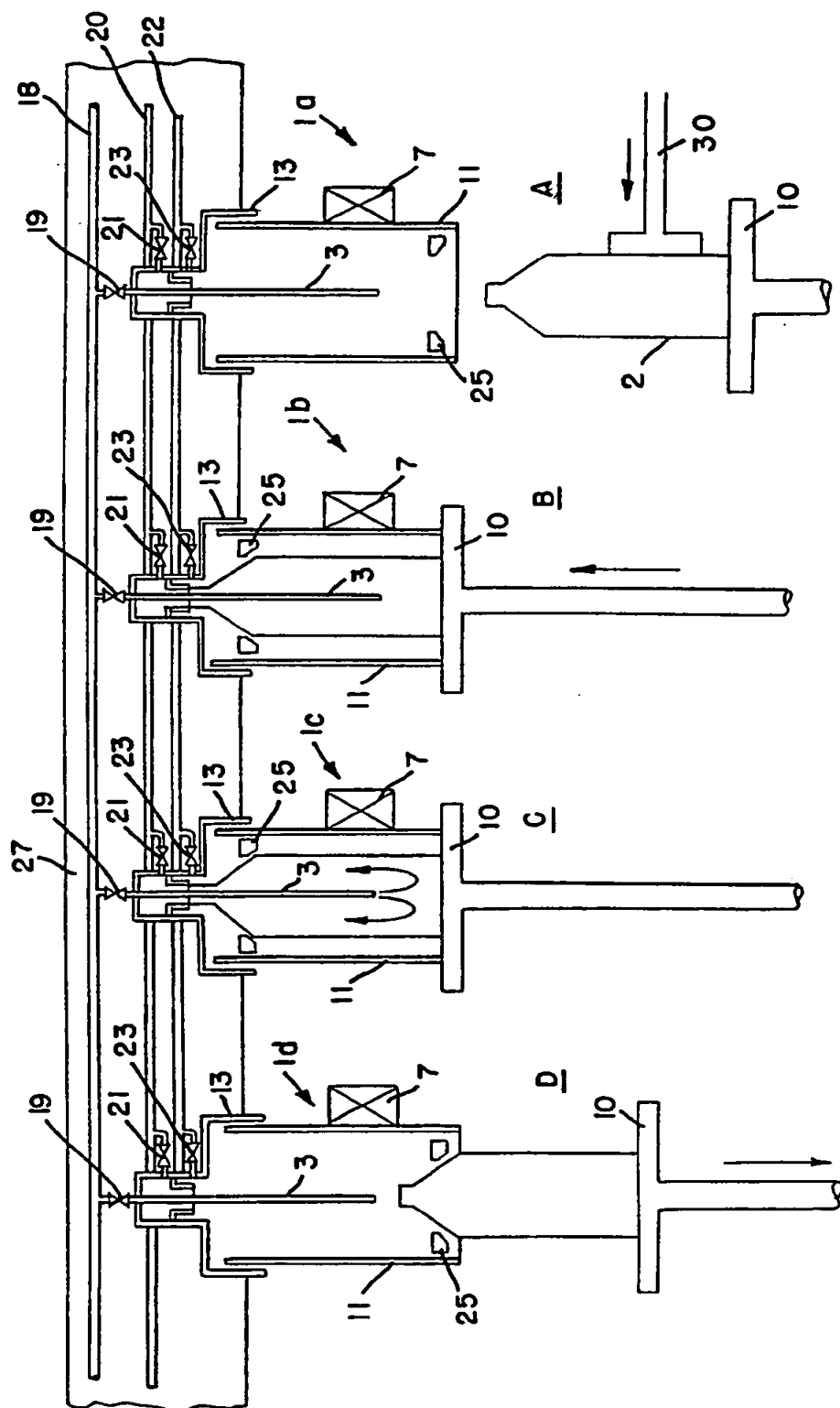


FIG. 3

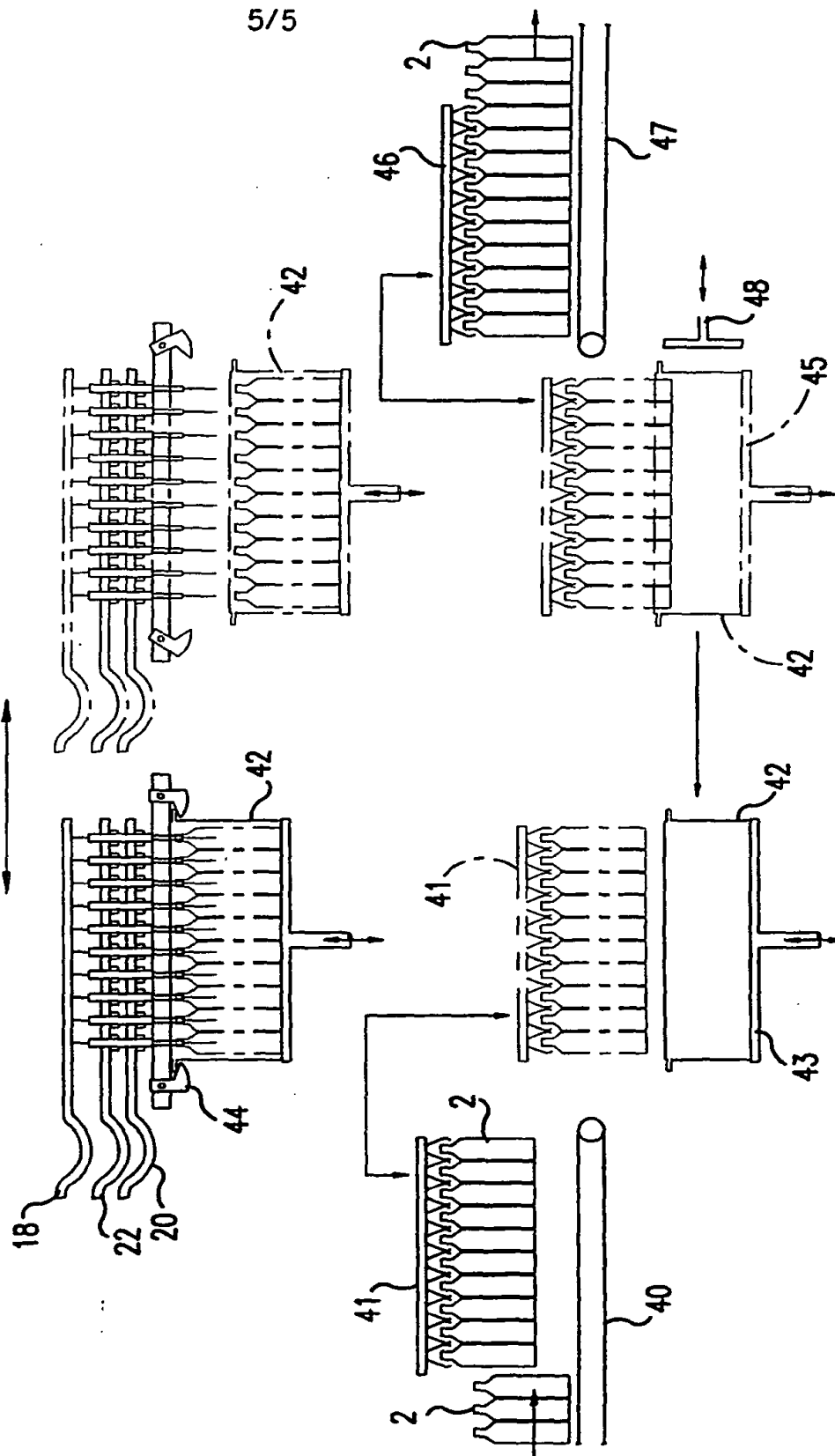


FIG. 4

INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/US 95/01645

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 B05D7/24 C23C16/04		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 B05D C23C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO,A,94 27745 (KAUTEX WERKE GMBH ;BUCK PLASMA ELECTRONIC GMBH (DE); ESSER KG KLAU) 8 December 1994 see claims; figures ---	1,4, 8-10, 12-14, 20-25, 28-30
X	WO,A,93 24243 (POLAR MATERIALS INC) 9 December 1993 see the whole document ---	13-26, 28-31
X	DE,A,36 32 748 (VER ZUR FÖRDERUNG DES INSTITUTS FÜR KUNSTSTOFFVERARBEITUNG) 7 April 1988 see the whole document ---	23,24, 28,29
-/--		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*&* document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center; font-weight: bold;">31 May 1995</div>		Date of mailing of the international search report <div style="text-align: center; font-weight: bold;">16.06.95</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016		Authorized officer <div style="text-align: center; font-weight: bold;">Brothier, J-A</div>

INTERNATIONAL SEARCH REPORT

Intern. Appl. No.
PCT/US 95/01645

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,39 08 418 (PLASMA ELECTRONIC GMBH) 20 September 1990 see the whole document ---	13-24, 28,29
A	GB,A,2 053 026 (WERTHEIMER M R;SCHREIBER H P) 4 February 1981 see the whole document -----	1-31

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No
PCT/US 95/01645

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9427745	08-12-94	DE-A- 4318084 DE-A- 4318086	08-12-94 08-12-94
WO-A-9324243	09-12-93	AU-B- 4403093 CA-A- 2112102 EP-A- 0601166 JP-T- 7502561 PL-A- 302309 US-A- 5378510	30-12-93 09-12-93 15-06-94 16-03-95 25-07-94 03-01-95
DE-A-3632748	07-04-88	NONE	
DE-A-3908418	20-09-90	NONE	
GB-A-2053026	04-02-81	NONE	